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## DEPOSITING METAL PARTICLES ON CARBON NANOTUBES

### BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

This invention relates to a method of depositing metal particles on carbon

5 nanotubes.

### DISCUSSION OF THE PRIOR ART

Carbon nanostructures have been used as metal catalyst supports in electrochemistry and fuel cells [see, for example H. Baughman et al, *Science*, **297**, 787 (2002), G. Che et al, *Langmuir*, **15**, 750 (1999), Z. Liu et al, *Langmuir*, **18**, 4054 (2002), W. Li et al, *Carbon*, **40**, 787 (2002), E.G. Steigerwalt et al, *J. Phys. Chem. B*, **106**, 760 (2002) and T. Yoshitake, et al, *Physica B*, **323**, 124 (2002)]. However, in the past, catalysts have been deposited on loose nanostructures, nanofibers and nanohorns just as on carbon black. When such carbon nanostructures were used in fuel cells, acceptable or better performance was always reported. However, it has been shown [see E.B. Easton et al, *Electrochem. Solid-State Lett.*, **3**, 359 (2000)] that when platinum on carbon black is used in fuel cells, only a fraction of the Pt-based catalyst is electrically connected to the backing electrode.

Carbon nanotubes are hydrophobic which makes it difficult for metal particles to adhere to them. E. Dujardin et al, *Science*, **265**, 1850 (1994) have reported that carbon nanotubes could not be wet by liquids with a surface tension higher than 100 - 200 mn/m which means that most metals would not adhere to them. In order to improve adhesion of metals to nanotubes, two main approaches have been proposed, namely surface modification and sensitization activation. The former involves oxidation of the nanotube surface in order to create functional groups and

increase metal nucleation [see Y.P. Sun et al, *Acc. Chem. Res.*, **35**, 1096 (2002) and T.W. Ebbesen et al, *Adv. Mater.*, **8** 155 (1996)]. Sensitization activation involves the generation of small nuclei, for example of Pd-Sn to promote metal deposits on carbon nanotubes [see Z. Liu et al, *supra* and L.M. Ang et al, *Carbon*, **38**, 363 (2000)]. However, a need still exists for an efficient method of depositing metals, and in particular metallic catalysts on carbon nanotubes.

#### GENERAL DESCRIPTION OF THE INVENTION

The object of the present invention is to meet the above-defined need by providing a simple method of depositing metal catalyst particles on carbon nanotubes and a carbon substrate which results in minimal contact resistance between the nanotubes and the substrate. The deposition of metal catalyst particles on nanotubes, which are themselves in electrical contact with a conductive carbon backing, is expected to dramatically improve catalyst utilization, especially at low catalyst loading.

#### GENERAL DESCRIPTION OF THE INVENTION

Accordingly, the present invention provides a process for producing carbon nanotubes with metallic catalyst particles thereon comprising the steps of:

- (a) preparing a silane solution of a metallic catalyst;
- (b) immersing an electrically conducting substrate carrying carbon nanotubes in the silane solution to yield a composite of substrate, carbon nanotube and metallic catalyst structure; and
- (c) reducing the composite structure to yield a composite of substrate, carbon nanotube and metallic catalyst particle structure.

## BRIEF DESCRIPTION OF THE DRAWINGS

The invention is described below in greater detail with reference to the accompanying drawings, wherein:

Figure 1 is a schematic reaction of silane derivative as used in the  
5 preparation of MWCNTs;

Figure 2 shows transmission electron micrographs (TEMs) of Pt nanoparticles  
on MWCNTs;

Figure 3 shows cyclic voltammograms in  $K_3Fe(CN)_6$  aqueous solutions of  
bare carbon paper substrate and MWCNTs deposited on carbon paper;

10 Figure 4 shows cyclic voltammograms in  $H_2SO_4$  (pH 1) of (A) bare carbon  
paper, (B) MWCNTs grown on carbon paper and (C) small Pt particles on MWCNTs;  
and

Figure 5 is a high resolution TEM of PtRu particles deposited on a carbon  
nanotube.

## 15 DESCRIPTION OF THE PREFERRED EMBODIMENT

Published US Patent Application 2003-0202930, which is incorporated herein  
by reference, describes a method of producing carbon nanotubes on carbon paper  
backing or substrate. As described in detail in the application, multi-walled carbon  
nanotubes (MWCNTs) were produced by heating Co-Ni particles deposited on the  
20 fibers of carbon paper in a specifically designed chemical vapor deposition (CVD)  
reactor. This reactor takes advantage of the fact that the carbon fuel cell backing  
(E-TEK, Division of DeNora with 81% porosity) is a conducting material, which is  
heated by the Joule effect up to 800°C, a temperature high enough to decompose  
ethylene and grow nanotubes. The surface polarity of the support can be modified

by methanol pretreatment of the support. Prior to Co-Ni deposition, the carbon backings were pretreated with methanol for 30 min, in order to improve the homogeneity of the Co-Ni particle sizes and their distributions on the carbon fibers of the backing. Details of Co-Ni particle deposition were described previously [X. Sun et al, *Chem. Phys. Lett.*, **363**, 415 (2002) and X. Sun et al, *International Journal of Nanoscience*, **1**, 223 (2002)]. As illustrated schematically in Fig. 1, an important step in the fabrication of the MWCNTs is the use of a commercially available silane derivative 2(4-chlorosulfonylphenyl) ethyl trichlorosilane available from United Chemical Technologies which, upon hydrolysis, forms a sulfonic acid-silicate, permitting the exchange of H<sup>+</sup> for Co<sup>2+</sup> and Ni<sup>2+</sup> ions. The latter ions are the precursors of the Co-Ni particles. Platinum deposition on nanotubes and the carbon paper substrate was effected using the same silane derivative, but using Pt<sup>2+</sup> ions as Pt particle precursors.

In the present case, a metal selected from the group consisting of platinum, palladium, titanium, ruthenium, gold, nickel, cobalt, silver, manganese, molybdenum and alloys thereof is deposited on the MWCNTs using a silane derivative.

### **Example 1**

In a preferred embodiment of the invention, Pt is deposited using 2(4-chlorosulfonylphenyl) ethyl trichlorosilane and platinum chloride. The MWCNT/carbon paper composite was immersed in a solution containing 0.04M PtCl<sub>2</sub>, 1 vol % silane derivative and 6 vol % water in ethanol. The composite structure was then dried at room temperature and reduced in a stream of H<sub>2</sub> + Ar at 580°C for 15 minutes. The 30 minute methanol pretreatment of the

MWCNTs/carbon paper composite described in the earlier published application was also used with success to improve the distribution of the Pt on the nanotubes.

A Hitachi-9000 NAR high-resolution transmission electron microscope (HRTEM), with energy dispersive X-ray spectroscopy (EDX), operated at 300 kV  
5 was employed to characterize the structure, composition and morphology of the resulting carbon nanotubes and Pt particles.

It is possible to deposit Pt particles on these nanotubes by simply adsorbing Pt ions for 2 hours from a Pt ion aqueous solution on methanol pretreated MWCNT/carbon paper. This procedure yields large (~ 4-10 nm) Pt particles after  
10 heat treatment in a reducing atmosphere, as shown in Fig. 2A. However, much smaller Pt particles (Fig. 2B) are obtained when Pt ions are dispersed on MWCNT/carbon paper using the silane derivative procedure (Fig. 1) to adsorb Pt ions onto the nanotubes. A magnified view of the homogeneous dispersion of the small Pt particles is presented in Fig. 2C, which also displays the graphitic structure  
15 of the nanotube walls, comprising 15 concentric graphene sheets. The tube has an outer diameter of nearly 35 nm with a hollow center of about 25 nm. The size of about 100 Pt particles was measured on a high resolution TEM micrography and an average Pt particle size of  $1.2 \pm 0.3$  nm was determined. The EDX compositional analysis of several Pt nanoparticles confirms the presence of Pt, along with a small  
20 amount of Co and Ni, which have their origin in the metals used as catalysts for the nanotube growth. An important point to stress is that neither S (a poison for Pt) nor Si signals were detected by EDX, with the Pt signal. It should also be noted that all Pt particles are located on the external surface of the tubes because the tubes were not opened. The density of the Pt particles, based on averaging the measurements

performed from HRTEM microographies on tubes, is nearly one particle/100 nm<sup>2</sup>.

Accordingly, if one typical nanotube is 20 µm long and 40 nm in diameter, it will be decorated with 2.5 × 10<sup>4</sup> Pt particles on its outer wall.

It is of practical importance for fuel cell applications to show that:

- 5            (i)      the MWCNTs are in electrical contact with the fuel cell backing  
              (ii)     the Pt particles are in electrical contact with MWCNTs.

The electrochemical properties of the electrode materials were investigated by cyclic voltammetry in a standard three-electrode cell. A Pt foil served as counter electrode, and a saturated calomel electrode (SCE) was used as reference 10 electrode. All working electrodes had the same 1 cm<sup>2</sup> of geometrical surface. Cyclic voltammetry measurements were carried out using a 273A EGG Potentiostat with a 10 mV/s sweep rate. Fe(CN)<sub>6</sub><sup>3-/4-</sup> were used as the oxydo-reduction couple (as a 10 mM solution of K<sub>3</sub>Fe(CN)<sub>6</sub> in 0.5M K<sub>2</sub>SO<sub>4</sub>) for the bare carbon paper and for the MWCNT/carbon paper electrodes. A H<sub>2</sub>SO<sub>4</sub> solution at pH 1, purged with Ar, was 15 used to perform the voltammetry of Pt particles deposited on MWCNT/carbon paper. For all those experiments, the voltammograms were recorded after cycling the working electrode at least 20 times, at 50 mV/s, in the same potential range as that used to record the voltammetry.

The electrical contact between MWCNTs and the carbon fibers of the fuel cell 20 backing is demonstrated in Fig. 3. This figure shows the voltammetry of the Fe(CN)<sub>6</sub><sup>3-/4-</sup> couple on a bare carbon paper and on MWCNTs grown on the carbon paper. A typical voltammogram with graphite features and a higher available electroactive surface is obtained on MWCNTs, strongly suggesting that these nanotubes are electrically connected to the carbon backing. The electrical contact

of Pt particles with MWCNTs is demonstrated, in Fig. 4, by the voltammetry occurring on Pt in an Ar purged H<sub>2</sub>SO<sub>4</sub> solution of pH 1. A comparison of voltammograms B, and C of Fig. 4 clearly show that the characteristic features of Pt surface electrochemistry, superimposed on a capacitive current, are seen in the 5 voltammogram displayed in C of Fig. 4. The latter voltammogram suggests that Pt particles are also electrically connected to the carbon nanotubes. Fig. 4C also displays the voltammogram of a commercial Pt electrode (ELAT™ from E-TEK, Inc.) for comparison

A short-time stability test for Pt particles on MWCNTs was performed by 10 immersing the electrode in H<sub>2</sub>SO<sub>4</sub> (pH 1) for 18 h. TEM observation of this electrode indicates that Pt particles are not removed by this treatment and that they maintain their small size. The MWCNTs remain also strongly bond to the carbon paper substrate.

### **Example 2**

15 PtRu alloy is currently the most popular catalyst used in polymer electrolyte fuel cells for the oxidation of hydrogen in the presence of several tens of ppm of CO. It is also the preferred catalyst used for the oxidation of methanol in direct MeOH fuel cells.

MWCNTs were synthesized on carbon paper at approximately 800°C from 20 the decomposition of ethylene on Co-Ni catalyst particles that were dispersed by a silane intermediate layer adsorbed onto the carbon fibers. Prior to depositing PtRu clusters on the carbon nanotube and carbon fiber composite, different pretreatments of the composite were effected to anchor the bimetallic particles to the tubes. The pretreatment includes (i) methanol immersion for 30 min, (ii) silane pyrolysis at

800°C under H<sub>2</sub> + Ar for 10 min or (iii) immersion in concentrated H<sub>2</sub>SO<sub>4</sub> + HN0<sub>3</sub> (50:50 vol) at 140°C for 5 min. Pretreatments (ii) and (iii) give a larger density of Pt-Ru alloy nanoparticles than pretreatment (i).

PtRu alloy was deposited on a MWCNT/carbon paper composite by immersing the composite for 2 hours in a solution containing 0.04 M PtCl<sub>2</sub>, 0.04 M RuCl<sub>2</sub>, 1 vol% of sulfonated silane, 6 vol % water and ethanol. The composite was then dried at room temperature and reduced in a flow of H<sub>2</sub> + Ar at 580°C for 15 min before examination by HRTEM. Figure 5 is a typical HRTEM image showing deposits of PtRu particles. The tube has an outer diameter of nearly 25 nm with a hollow (inner diameter) of about 13 nm. The walls of the tube consist of about 15 cylindrical graphene layers. Nanoparticles are clearly seen to decorate the MWCNTs and they are evenly distributed over the walls of the tubes. The particles are located only on the external surfaces of the tubes, because the tubes were not opened by the pretreatments, even the short immersion in concentrated H<sub>2</sub>SO<sub>4</sub> + HNO<sub>3</sub>. The particle size distribution is quite narrow, with an average size of less than 1.5 nm.